

Fokker-Planck-Boltzmann equation for dissipative particle dynamics

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Abstract

The algorithm for Dissipative Particle Dynamics (DPD), as modified by Español and Warren, is used as a starting point for proving an H -theorem for the free energy and deriving hydrodynamic equations. Equilibrium and transport properties of the DPD fluid are explicitly calculated in terms of the system parameters for the continuous time version of the model.

PACS. 05.20 Dd Kinetic theory; 05.70 Ln Nonequilibrium thermodynamics, irreversible processes; 47.11+j Computational methods in fluid dynamics.

In recent years several new simulation methods have been proposed for studying dynamical and rheological properties of complex fluids, on time scales which are difficult to reach by conventional molecular dynamics methods. These new techniques include lattice gas cellular automata (LGCA), the lattice Boltzmann equation (LBE), and dissipative particle dynamics (DPD).

The goal of this letter is a theoretical analysis of the equilibrium and transport properties of a DPD system. This method was introduced by Hoogerbrugge and Koelman [1] and modified by Español and Warren [2] to ensure a proper thermal equilibrium state. There exist many recent applications of this new technique to concentrated colloidal suspensions, dilute polymer solutions and phase separation in binary mixtures [3]. Of course, to study the rheology of colloidal particles and polymers, suspended in a DPD fluid, one needs to model in addition the hydrodynamic interactions between these objects, transmitted through the fluid [3], which is not the goal of this article.

We briefly recall the basic elements of the simulation method. The DPD particle-based algorithm considers N point particles which model a fluid out of equilibrium and conserve mass and momentum, but not energy. Positions and velocities are continuous, but time is discrete and incremented in time steps δt , as in LGCA and LBE. The algorithm consists of a collision step and a propagation step. In the *collision step*, the velocity of each particle is updated according to its interaction with particles inside a sphere of radius R_0 through conservative, frictional and random forces. In the subsequent *propagation* step of fixed length δt all particles move freely to their new positions.

The equations of motion for DPD with a finite step δt are given by [1]

$$\begin{aligned} \mathbf{v}_i(t + \delta t) - \mathbf{v}_i(t) &= \mathbf{a}_i(t, \delta t) \equiv \sum_{j(\neq i)} \{ \mathbf{k}_{ij} \delta t + \boldsymbol{\sigma}_{ij} \delta W_{ij} \} \\ \mathbf{r}_i(t + \delta t) - \mathbf{r}_i(t) &= \mathbf{v}_i(t + \delta t) \delta t, \end{aligned} \quad (1)$$

where $x_i = \{\mathbf{v}_i, \mathbf{r}_i\}$ is the phase of the i -th particle ($i = 1, 2, \dots, N$). The interparticle force contains a systematic part \mathbf{k} and a random part $\boldsymbol{\sigma} \delta W$. The systematic force $\mathbf{k}_{ij} = \mathbf{F}_{ij}/m - \boldsymbol{\gamma}_{ij}$ has a conservative part $\sim \mathbf{F}$ and a dissipative part $\boldsymbol{\gamma}$. The random force is described by a stochastic variable δW , defined through $\delta W_{ij} = \int_t^{t+\delta t} d\tau \xi_{ij}(\tau)$, where $\xi_{ij}(t)$ is Gaussian white noise with an average $\bar{\xi}_{ij} = 0$ and a correlation $\overline{\xi_{ij}(t)\xi_{kl}(t')} = (\delta_{ik}\delta_{jl} + \delta_{il}\delta_{jk})\delta(t - t')$, and $\delta(t)$ is a Dirac delta function. The forces are defined as $\mathbf{F}_{ij} = -\partial\phi(R_{ij})/\partial\mathbf{r}_i$, $\boldsymbol{\gamma}_{ij} = \gamma w_D(R_{ij}) \widehat{\mathbf{R}}_{ij} \widehat{\mathbf{R}}_{ij} \cdot (\mathbf{v}_i - \mathbf{v}_j)$ and $\boldsymbol{\sigma}_{ij} = \sigma w_R(R_{ij}) \widehat{\mathbf{R}}_{ij}$, where $\phi(R)$ is a pair potential, $w_D(R)$ and $w_R(R)$ are positive weight functions, and γ and σ are respectively the strength of the friction and the noise. The weight function vanishes outside a finite range R_0 (here chosen to be equal for w_D and w_R). Moreover, $\mathbf{R}_{ij} = \mathbf{r}_i - \mathbf{r}_j$, and a hat denotes a unit vector.

The interparticle forces \mathbf{k}_{ij} , \mathbf{F}_{ij} , $\boldsymbol{\gamma}_{ij}$ and $\boldsymbol{\sigma}_{ij}$ are antisymmetric under interchange of i and j , which guarantees the conservation of total momentum, which is a prerequisite for the existence of a slowly changing local fluid velocity and the validity of the Navier Stokes equation.

Formally, the DPD algorithm defines a microscopic N particle system. However, the introduction of noise and dissipation represents a coarse grained description. Consequently, the “DPD particles” should not be interpreted as molecules, but as some mesoscopic degree of freedom of the fluid, referred to as “lumps.” If $t_0 \propto 1/\gamma n R_0^d$ denotes the characteristic molecular time scale in DPD with $n = N/V$ the number density, d the number of dimensions and γ the friction constant, then t_0 is considered to be large compared to any molecular time scale. In this description the *dominant* interactions are friction ($\sim \gamma$) and random noise ($\sim \sigma$), whereas the conservative forces can be interpreted as *weak* forces of relatively long range, which can be treated perturbatively. At sufficiently small temperature, they are responsible for phase transitions from liquid to crystalline order. Here they will be set equal to zero (γ large). The random forces act effectively as repulsive forces to prevent collapse of DPD particles.

Define the single particle and pair distribution functions as

$$f(x, t) = \langle \sum_i \delta(x - x_i(t)) \rangle; \quad f^{(2)}(x, x', t) = \langle \sum_{i \neq j} \delta(x - x_i(t)) \delta(x' - x_j(t)) \rangle, \quad (2)$$

where $\langle \dots \rangle$ represents an average over an initial ensemble of the N -particle system. Combination of (2) and (1) then yields:

$$\begin{aligned} f(\mathbf{v}, \mathbf{r} + \mathbf{v}\delta t, t + \delta t) &= \langle \sum_i \delta(\mathbf{r} - \mathbf{r}_i(t)) \delta(\mathbf{v} - \mathbf{v}_i(t) - \mathbf{a}_i(t)) \rangle \\ &= \langle \sum_i [1 - \mathbf{a}_i \cdot \boldsymbol{\partial} + \frac{1}{2} \mathbf{a}_i \mathbf{a}_i : \boldsymbol{\partial} \boldsymbol{\partial} + \dots] \delta(x - x_i(t)) \rangle \end{aligned} \quad (3)$$

where $\boldsymbol{\partial} = \partial/\partial \mathbf{v}$ is a gradient in the \mathbf{v} -variable and $(:)$ denotes a double contraction. As the total force \mathbf{a}_i is small for small δt , the argument of the δ -function may be expanded in powers of \mathbf{a}_i . A subsequent average over the random noise gives,

$$f(\mathbf{v}, \mathbf{r} + \mathbf{v}\delta t, t + \delta t) - f(\mathbf{v}, \mathbf{r}, t) = \delta t \mathcal{J}_1(f) + (\delta t)^2 \mathcal{J}_2(f) + \mathcal{O}((\delta t)^3) + \dots, \quad (4)$$

where the *collision* terms $\mathcal{J}_1(f)$ and $\mathcal{J}_2(f)$ can be calculated straightforwardly. Here we only quote the dominant term of $\mathcal{O}(\delta t)$ explicitly:

$$\mathcal{J}_1(f) = \boldsymbol{\partial} \cdot \int dx' \mathbf{k}(x, x') f^{(2)}(x, x') + \frac{1}{2} \boldsymbol{\partial} \boldsymbol{\partial} : \int dx' \boldsymbol{\sigma}(x, x') \boldsymbol{\sigma}(x, x') f^{(2)}(x, x'). \quad (5)$$

The term $\mathcal{J}_2(f)$ contains $\mathcal{O}(\partial^n)$ with $n = 2, 3, 4$ and involves the higher order distribution functions $f^{(2)}$ and $f^{(3)}$. Equation (4) constitutes the first equation of the BBGKY-hierarchy for the DPD fluid with discrete time steps, relating the change in f to higher order distribution functions.

To obtain a closed kinetic equation for $f(x, t)$, the so-called the Fokker-Planck-Boltzmann (FPB) equation, we assume *molecular chaos*, i.e. $f^{(2)}(x, x', t) = f(x, t)f(x', t)$, etc. The dominant collision term (5) contains the systematic frictional force as well as the random force. Next consider the *propagation term*, which is the lhs of (4). In the limit of small δt it simplifies to the usual streaming term $\partial_t f + \mathbf{v} \cdot \nabla f$, and the FPB equation becomes

$$\partial_t f(x) + \mathbf{v} \cdot \nabla f(x) = I(f). \quad (6)$$

Here $\nabla = \partial/\partial \mathbf{r}$ is a spatial gradient and the collision term becomes:

$$I(f) = \boldsymbol{\partial} \cdot \int dx' \boldsymbol{\gamma}(x, x') f(x') f(x) + \frac{1}{2} \boldsymbol{\partial} \boldsymbol{\partial} : \int dx' \boldsymbol{\sigma}(x, x') \boldsymbol{\sigma}(x, x') f(x') f(x). \quad (7)$$

We will concentrate on the case of continuous time. The most fundamental properties of the FPB equation are: it conserves particle number $N = \int dx f(x, t)$ and total momentum $P = \int dx \mathbf{v} f(x, t)$, and obeys an *H*-theorem, $\partial_t \mathcal{F} \leq 0$, for the total free energy: $\mathcal{F}(f) = \int dx \{ \frac{1}{2} m v^2 + \theta_0 \ln f(x) \} f(x)$, provided the *detailed balance* conditions [2], $\theta_0 = m\sigma^2/2\gamma$ and $w_D(r) = w_R^2(r) \equiv w(r)$, are satisfied. The constant θ_0 depends only on the model parameters. In absence of conservative forces, the *H*-theorem implies the existence of a unique equilibrium solution, $f_0(x) = n_0 \varphi_0(v)$ where $\varphi_0(v) = (m/2\pi\theta_0)^{d/2} \exp[-\frac{1}{2}mv^2/\theta_0]$ is a Maxwellian, and $n_0 = N/V$ is the density. If the detailed balance conditions are violated, the proof of the *H*-theorem breaks down. The modified algorithm [2] satisfies the detailed balance conditions in the limit $dt \rightarrow 0$, but the original one [1] does not.

Our goal here is to derive the macroscopic evolution equations, describing the fluid dynamics on large spatial and temporal scales, i.e. the Navier-Stokes equation, and to obtain explicit expressions for the thermodynamic and transport properties in terms of density n , temperature θ_0 , friction γ and range R_0 .

As the interactions in the DPD fluid do not conserve energy, only mass density, $\rho(\mathbf{r}, t) = mn(\mathbf{r}, t) = \int d\mathbf{v} f(\mathbf{r}, \mathbf{v}, t)$, and momentum density $\rho(\mathbf{r}, t)\mathbf{u}(\mathbf{r}, t) = \int d\mathbf{v} f(\mathbf{r}, \mathbf{v}, t)\mathbf{v}$, satisfy local conservation laws, where $\mathbf{u}(\mathbf{r}, t)$ is the local flow velocity of the fluid. The approach to equilibrium proceeds in two stages: first, a rapid relaxation (*kinetic stage*) to local equilibrium within a characteristic kinetic relaxation time t_0 . The energy density $e(\mathbf{r}, t)$ decays within the same short kinetic stage to $\frac{1}{2}d\theta_0 n(\mathbf{r}, t)$, where θ_0 is the global equilibrium temperature $\theta_0 = k_B T_0$. In the subsequent *hydrodynamic stage* the time evolution of $f(x, t)$ in the DPD fluid is only determined by the slow fields $n(\mathbf{r}, t)$ and $\mathbf{u}(\mathbf{r}, t)$, i.e. $f(\mathbf{v}|n(\mathbf{r}, t), \mathbf{u}(\mathbf{r}, t))$,

but the temperature is thermostated at the global equilibrium value θ_0 . All processes proceed isothermally. As a DPD fluid is not able to sustain a temperature gradient on hydrodynamic time scales, there is no heat current proportional to a temperature gradient and there is no heat conductivity.

Using the Chapman-Enskog method [5], f can be determined perturbatively, $f = f_0 + \mu f_1 + \dots$, as an expansion in powers of a small parameter, $\mu \sim \ell_0 \nabla$, which measures the variation of the macroscopic parameters over the characteristic kinetic length scale, $\ell_0 = \bar{v}t_0 \propto \bar{v}/\gamma n$ with $\bar{v} = \sqrt{\theta_0/m}$ the mean velocity. The first term f_0 is the local equilibrium distribution, $f_0 = n(\mathbf{r}, t) (m/(2\pi\theta_0))^{d/2} \exp[-m(\mathbf{v} - \mathbf{u}(\mathbf{r}, t))^2/(2\theta_0)]$. The next term f_1 , linear in the gradients, is obtained as the solution of $\partial_t f_0 + \mathbf{v} \cdot \nabla f_0 = (dI_0/df)_{f_0} f_1$, where the time derivatives $\partial_t n$ and $\partial_t \mathbf{u}$ are eliminated using the lowest order hydrodynamic equations (Euler equations). So, we first need to consider the local conservation laws.

Integration of (6) over \mathbf{v} yields at once the continuity equation, $\partial_t n = -\nabla \cdot n \mathbf{u}$. Similarly, we derive the conservation law for the momentum density by multiplying (6) by \mathbf{v} and by integrating over \mathbf{v} . The result after a partial \mathbf{v} - integration is

$$\begin{aligned} \partial_t \rho \mathbf{u} &= -\nabla \cdot \int d\mathbf{v} \mathbf{v} \mathbf{v} f(x) - m \int d\mathbf{v} dx' \boldsymbol{\gamma}(x, x') f(x') f(x) \\ &\equiv -\nabla \cdot (\rho \mathbf{u} \mathbf{u} + \mathbf{\Pi}_K + \mathbf{\Pi}_D). \end{aligned} \quad (8)$$

The kinetic part of the pressure tensor is the momentum flux in the local rest frame of the fluid $\mathbf{\Pi}_K = \int d\mathbf{v} m \mathbf{v} \mathbf{v} f - \rho \mathbf{u} \mathbf{u} = \int d\mathbf{v} m \mathbf{V} \mathbf{V} f$, where $\mathbf{V} = \mathbf{v} - \mathbf{u}(\mathbf{r}, t)$ is the *peculiar* velocity. Substitution of $f = f_0 + \mu f_1$ gives to lowest order $\mathbf{\Pi}_K \simeq n\theta_0 \mathbb{I} + \mathcal{O}(\mu)$, where $n\theta_0$ is the local equilibrium pressure. The next term on the rhs of (8) defines the *dissipative* part $\mathbf{\Pi}_D$ of the momentum flux. It reduces to

$$\nabla \cdot \mathbf{\Pi}_D = m\gamma \int d\mathbf{R} w(R) \widehat{\mathbf{R}} \widehat{\mathbf{R}} \cdot (\mathbf{u}(\mathbf{r}) - \mathbf{u}(\mathbf{r}')) n(\mathbf{r}) n(\mathbf{r}'), \quad (9)$$

where $\mathbf{r}' = \mathbf{r} - \mathbf{R}$. It is a typical *collisional transfer* contribution, resulting from the non-locality of the collision operator [5]. Expansion of $\mathbf{u}(\mathbf{r}')$ and $n(\mathbf{r}')$ around \mathbf{r} shows that the rhs of (9) is $\mathcal{O}(\mu^2)$. It contributes to the viscosities but not to the Euler equations. After some algebra we obtain $\mathbf{\Pi}_D = -2\eta_D \mathbf{D} - \zeta_D \nabla \cdot \mathbf{u} \mathbb{I}$, where the dissipative parts of the shear and bulk viscosity are identified as:

$$\eta_D = mn\omega_0 \langle R^2 \rangle_w / 2(d+2) \quad ; \quad \zeta_D = mn\omega_0 \langle R^2 \rangle_w / 2d. \quad (10)$$

where we define the kinetic relaxation rate $\omega_0 \equiv 1/t_0 = (n\gamma/d)[w]$ with $[w] = \int d\mathbf{R} w(R)$ the effective volume of the action sphere, and where $\langle R^2 \rangle_w = [R^2 w]/[w^2]$ is of order R_0^2 .

Following the standard Chapman-Enskog scheme, the solution f_1 is found to be proportional to $\nabla \mathbf{u}$. The corresponding part of the kinetic pressure tensor then has the form

$$\Pi_{K,1} = \int d\mathbf{v} m \mathbf{V} \mathbf{V} f_1 = -2\eta_K D - \zeta_K \nabla \cdot \mathbf{u} \mathbb{I}, \quad (11)$$

where the rate of shear tensor $D_{\alpha\beta}$ is defined as the traceless symmetric part of $\nabla_\alpha \mathbf{u}_\beta$. For the kinetic part of the viscosities we obtain the explicit results

$$\eta_K = n\theta_0/2\omega_0 \quad ; \quad \zeta_K = n\theta_0/d\omega_0, \quad (12)$$

which are new results. The final transport coefficients are then $\eta = \eta_D + \eta_K$ and $\zeta = \zeta_D + \zeta_K$. For further details we refer to [6].

The contribution η_D is *identical* to the estimate for the total shear viscosity of the DPD fluid, calculated in [1] on the basis of the continuum approximation to the equations of motion for the DPD particles. Hoogerbrugge and Koelman have also shown that the viscosity found in numerical simulations does indeed approach η_D for large values of $n\gamma$. Here we have confirmed and rederived the formula for the viscosity of [1] within a kinetic theory context.

We conclude this paragraph by listing the complete results for the viscosities of the DPD fluid in the continuous case ($\delta t \rightarrow 0$),

$$\eta = \frac{1}{2}n\theta_0 \left\{ \frac{\omega_0 t_w^2}{(d+2)} + \frac{1}{\omega_0} \right\} \quad ; \quad \zeta = \frac{1}{d}n\theta_0 \left\{ \frac{\omega_0 t_w^2}{2} + \frac{1}{\omega_0} \right\}. \quad (13)$$

The traversal time of an action sphere t_w is defined through $t_w^2 = m\langle R^2 \rangle_w / \theta_0 = \langle R^2 \rangle_w / \bar{v}^2$. The expressions for the transport coefficients (13) involve the two intrinsic time scales of the DPD fluid: the characteristic kinetic time $t_0 = 1/\omega_0$, and the traversal time t_w which is of order R_0/\bar{v} . In the parameter range $t_w > t_0$, the dissipative viscosities η_D and ζ_D dominate and the estimate of [1] is a reasonable one. In the range $t_w < t_0$ the kinetic viscosities η_K and ζ_K dominate. In a similar way the coefficient of self-diffusion D is obtained as $D = \theta_0/\omega_0 m$.

Results of numerical simulations for the kinematic viscosity $\zeta/(nm)$ show [6] that the theoretical results correctly describe the large and small $\omega_0 \sim n\gamma$ dependence, but a background contribution, roughly independent of ω_0 seems to be lacking in the theoretical predictions. There may be several reasons for this discrepancy, which are currently under investigation:

- (i) Effects of the discreteness of δt , which alter the equilibrium temperature [4].
- (ii) Poor convergence of the Chapman-Enskog expansion, resulting from a poor separation of the “fast” kinetic and “slow” hydrodynamic timescales.
- (iii) The system size L , measured in units of the interaction range R_0 , as used in the simulations of [6], may be too small and one is observing finite size effects related to wavenumber dependent transport coefficients (generalized hydrodynamics).

(iv) Breakdown of the stosszahlansatz, caused by the *small* net momentum transfer in DPD collisions. Consequently, dynamic correlations, built up by sequences of correlated binary (“ring”) collisions, may not be negligible.

The main results of the present paper are the explicit predictions for the viscosities and self-diffusion coefficient of the DPD fluid in terms of the model parameters: density n , friction γ , noise strength σ or equivalently temperature $\theta_0 = m\sigma^2/2\gamma$ and range R_0 . The expressions for η and ζ essentially depend on the two intrinsic time scales of DPD: the characteristic kinetic relaxation time t_0 and the traversal time t_w of the action sphere.

The method used in eqs. (2-4) for deriving equations of motion for the reduced distribution functions, can be directly applied to the N -particle distribution function, $P(y_1, y_2, \dots, y_N, t) = \langle \prod_{i=1}^N \delta(y_i - x_i(t)) \rangle$, and yields the discrete time analog of the N -particle Fokker-Planck equation for continuous time [2]. Our equation for finite step size reduces to the Fokker-Planck equation of [2] in the limit $\delta t \rightarrow 0$.

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